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A new *C*-glycosyl xanthone isolated from *Davallia solida*

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Abstract

A new xanthone glycoside has been isolated together with mangiferin from *Davallia solida*. The structures were elucidated by chemical and spectral means as 2-*C*-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (mangiferin, **1**) and 2-*C*-β-D-xylopyranosyl-1,3,6,7-tetrahydroxyxanthone (**2**). © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Davallia solida (Forst.) Swartz is a fern widely distributed in the West Pacific islands and used in folk medicine for ciguatera treatment (in New Caledonia, Vanuatu) as well as analgesic and purgative (in other Pacific islands) (Bourdy, Cabalion, Amade & Laurent, 1992). Only one study has shown the presence of mangiferin (**1**) in this fern on the basis of paper chromatography results (Richardson, 1983). In the present paper, we confirm the presence of (**1**) by spectroscopic methods and describe the isolation and identification of a new *C*-xylosyl-xanthone (**2**).

2. Results and discussion

Air-dried rhizomes were sequentially extracted with solvents of increasing polarities. The evaporated methanolic and methanol-water extracts were taken up in water and partitioned against chloroform and *n*-butanol. From the latter extract, a precipitate was obtained, which was then purified by preparative TLC leading to mangiferin (**1**). The supernatant, submitted to a combination of CC led to the isolation of 2-*C*-β-D-xylopyranosyl-1,3,6,7-tetrahydroxyxanthone (**2**). UV spectra in methanol and classic reagents for compounds **1** and **2** were characteristic for a xanthone with free hydroxyl groups at positions C-1 and C-3 and with an *ortho*-dihydroxylation pattern (Hostettmann & Hostettmann, 1989; Lins Mesquita, De Barros Corrêce, Gottlieb & Taveira Magahhades, 1968). The molecular formulae $C_{19}H_{18}O_{11}$ and $C_{18}H_{16}O_{10}$, for **1** and **2** respectively, were deduced from FABMS, ^{1}H and ^{13}C NMR data. FABMS, ^{1}H NMR, UV data and chromatographic behaviour of **1** were similar to those of reference mangiferin.

The FABMS spectra of **2** showed quasi-molecular ion peaks at *m/z* 415 $[M+Na]^+$, 393 $[M+H]^+$ and *m/z* 427 $[M+Cl]^-$, 391$[M-H]^-$ in positive and negative mode respectively, in accordance with a tetrahydroxy-*C*-pentosylxanthone.

The ^{13}C NMR spectrum of **2** showed 18 carbon atom signals. The presence of a glycosyl part was indicated by five peaks between 70–80 ppm. In the ^{1}H NMR spectrum, this sugar moiety showed signals in the 3–4.5 ppm range. The 2D COSY experiment clearly demonstrated the glycosidic chaining and the 2D HSQC map indicated that all sugar carbon atoms

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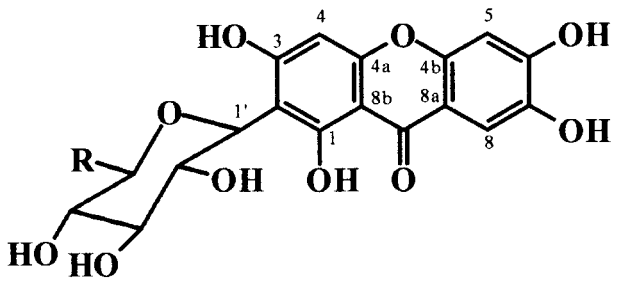

1 R = CH_2OH
2 R = H

1

were in the 70–80 ppm range. The pentose was identified as β-D-xylopyranose on the basis of its ^1H and ^{13}C NMR data (Agrawal, 1989, 1992). Acid hydrolysis of compound **2** did not release the pentose and the mass spectra did not show the usual fragmentation pattern for *O*-glycosides derivatives. These data together with the chemical shifts of H-1′ and C-1′ unambiguously showed the *C*-linkage of the sugar.

The ^{13}C NMR spectrum of **2** also showed three shielded aromatic methine groups at δ 94.0 (C-4); δ 103.5 (C-5) and δ 108 (C-8) ppm respectively. Among the ten quaternary carbon atom signals noted in the HSQC map, six corresponded to *O*-linked aromatic carbon atoms (145–165 ppm), while the peak at δ 180.0 ppm indicated the presence of a carbonyl function (Breitmayer & Voelter, 1989).

The 2D NMR experiments clearly showed that there was only one aromatic proton on the A-ring. The substitution pattern of B-ring was clearly indicated by the two singlets at δ 6.87 (H-5) and δ 7.38 (H-8). This was confirmed by the HMBC ^2J correlations noted between H-5 (δ 6.87) and the carbon atoms at δ 151.6 (C-6) and δ 154.9 (C-4b), and between H-8 (δ 7.38) and the signals at δ 112.6 (C-8a) and δ 144.6 (C-7). Moreover, the 6,7-*ortho*-dihydroxylation pattern of B-ring was confirmed by the reciprocal shielding of C-6 and C-7 at δ 151.6 and δ 144.6, respectively. Furthermore, ^{13}C chemical shifts of the genin of **2** were in accordance with those noted in the literature for tetrahydroxyxanthones (Frahm & Chaudhuri, 1979).

Finally, the cross peaks noted in the HMBC experiment between H-1′ (δ 4.50) and the carbon atoms C-2 (δ 108.5), C-1 (δ 162.8) and C-3 (δ 164.7) indicated unambiguously the linkage between the xylosyl moiety and the aglycone part. Thus, compound **2** was identified to 2-*C*-β-D-xylopyranosyl-1,3,6,7-tetrahydroxyxanthone a new natural product.

Table 1
NMR data for compound **2** at 125 MHz (^{13}C and DEPT) and 500 MHz (^1H) in CD_3OD

Position	^1H	^{13}C/HSQC
1-OH	13.77 *s*	162.8
2		108.5
3		164.7
4	6.37 *s*	94.0
4a		157.1
4b		154.9
5	6.87 *s*	103.5
6		151.6
7		144.6
8	7.38 *s*	108.9
8a		112.6
8b		102.1
CO		180.0
1′	4.50 *d* (9.8)	74.8
2′	4.08 *br t*	70.9
3′	3.13 *t* (8.8)	80.1
4′	ca 3.40 *m*	70.9
5′a	3.06 *t* (10.9)	71.2
5′b	3.75 *dd* (10.1; 5.0)	

3. Experimental

3.1. Plant material

Davallia solida (Forst.) Swartz was collected and identified by ORSTOM. A specimen is deposited at the Pharmacognosy Department (Laboratory of Pharmacognosy, Faculty of Pharmacy, 8 Avenue Rockefeller, 69373 Lyon Cedex 08, France).

3.2. General

Analyti. TLC: precoated silica gel 60F-254 plastic

Table 2
HMBC data for compound **2**

^{13}C	^1H								
	1-OH	4	5	8	1′	2′	3′	4′	5′a/b
1	^2J				^3J				
2	^3J	^3J			^2J				
3		^2J			^3J				
4a		^2J							
4b			^2J	^3J					
5									
6			^2J	^3J					
7			^3J	^2J					
8a			^3J	^2J					
8b	^3J	^3J							
CO				^3J					
1′						^2J	^3J		^3J
2′					^2J		^2J		
3′					^3J	^2J		^2J	^3J
4′							^2J		^2J
5′							^3J	^2J	

and glass sheets (Merck); analyti. HPLC: Merck Lichrospher 5 μm RP18 (250 × 4.6 mm); Waters μBondapak C18 10 μm (300 × 3.9 mm) and UV detection; prep. TLC: cellulose Macherey–Nagel 301; prep. MPLC: Merck Lichroprep RP18 40–63 μm (460 × 36 mm); Sephadex Pharmacia column (LH-20, 850 × 75 mm). Chromatographic mobilities were recorded in three systems: system 1 (cellulose, HOAc–H_2O, 3:17); system 2 [Waters μBondapak C18 (10 μm, 300 × 3.9 mm), MeOH-H_2O (1 ml/min; 5–75% MeOH in 15 min then isocratic)]; system 3 [Merck Lichrospher 100RP18 5 μm (250 × 4.6 mm), MeOH–H_2O (1 ml/min; 5–75% MeOH in 15 min)]. NMR: 500 MHz for ^1H and 125 MHz for ^{13}C were recorded on a Brücker DRX 500. The solvent signal was used as ref. (δ 3.32 and 49.0 for CD_3OD). Complete proton and carbon assignments were based on 1D ^1H and ^{13}C standard, 2D ^1H–^1H COSY, ^1H–^{13}C HSQC and ^1H–^{13}C HMBC NMR experiments (Tables 1 and 2). FAB-mass spectra were recorded on a Nermag R10-10C spectrometer. Acid hydrolysis was performed in 2N HCl under reflux.

3.3. Extraction and isolation

Dried and powdered rhizomes (500 g) were extracted with CH_2Cl_2, then with boiling MeOH and boiling MeOH–H_2O (1:1). The two last extracts were combined and concentrated, leading to a residue. The latter was solubilized in H_2O and partitioned against $CHCl_3$ and *n*-BuOH. In the *n*-BuOH layer, a precipitate of compound **1** appeared, which was then purified by prep. TLC (cellulose) using HOAc–H_2O (3:17) as solvent (R_f: 0.42). The supernatant was chromatographed on Sephadex LH-20 using MeOH as mobile phase. Five frs. (85 ml) were collected. The second one, after removal of the solvent under reduced pressure was submitted to a reverse phase MPLC using aq. MeOH (linear gradient) as solvent. The fr. eluted with 50% aq. MeOH afforded 31 mg of pure compound **2**.

3.3.1. Mangiferin (*1*)

UV λ_{max}^{MeOH} nm: 237, 254, 268sh, 312, 364; $+AlCl_3$: 235, 268, 321sh, 350, 390; $+AlCl_3+HCl$: 226, 259, 276sh, 316, 331, 398; +NaOH: 235, 268, 297sh, 340, 388; +NaOAc: 237, 263, 300sh, 334, 394; FAB^+MS (thioglycerol) (*m/z*): 423 $[M+H]^+$; FAB^-MS (thioglycerol) (*m/z*): 421 $[M-H]^-$; ^1H NMR (500 MHz) (δ ppm, *J* Hz): 3.45 (H-3′, H-4′, H5′, overlapping signals), 3.74 (H-6′a, *dd*, 12.0; 5.0), 3.88 (H-6′b, *dd*, 12.0; 2.0), 4.19 (H-2′, *t*, 9.4), 4.94 (H-1′, *d*, 8.6), 6.37 (*s*, H-4), 6.77 (*s*, H-5), 7.60 (*s*, H-8). Chromatographic behaviour: R_f 0.32 (system 1); R_t 15.4 min (system 2).

3.3.2. 2-C-β-D-xylopyranosyl-1,3,6,7-tetrahydroxyxanthone (*2*)

UV λ_{max}^{MeOH} nm: 240, 257, 315, 363; $+AlCl_3$: 235, 265, 357, 385, 426sh; $+AlCl_3+HCl$: 233, 261, 337, 402; +NaOH: 244, 270, 302, 370, 390; +NaOAc: 239, 264, 340, 389; $+NaOAc+H_3BO_3$: 229, 261, 320, 370; FAB^+MS (glycerol + NaCl) (*m/z*): 415 $[M+Na]^+$, 393 $[M+H]^+$; FAB^-MS (glycerol + NaCl) (*m/z*): 427 $[M+Cl]^-$, 391$[M-H]^-$; ^1H and ^{13}C NMR data: see Table 1. Chromatographic behaviour: R_f 0.20 (system 1); R_t 11.3 min (system 3).

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